Mechanical Poperties of TiN/NbN Multilayered Films Prepared by PVD Coating

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Abstract

The TiN/NbN multilayered thin films using D.C. magnetron sputtering techniques have been studied. These are multilayer coatings with up to 8-64 layers, composing generally of arrangements of two materials of TiN and NbN. XRD analysis shows the TiN/NbN multilayered thin films of novel composite materials are constituted of crystalline structure and strong preferred orientation. Proper material selection and the adjustment of number of the layers can be contributed to an exceptionally enhancing of the mechanical properties and hardness values. On mechanical properties, Young's modulus and hardness values were enhanced progressively for layers number increase. The TiN/NbN multilayer films with alternating layers at 64 layers films exhibit the highest nano-hardness and best Young's modulus. It shows lowest friction coefficient and excellent wear resistance against steel ball.

Keywords

TiN/NbN; D.C. Magnetron Suttering; Young's Modulus

Introduction

Ceramic coatings composed of transition metal nitrides, such as TiN, TiAlN, CrN and NbN, have been largely in applied industry practice for the cutting tools, molds for the die casting and for various optical produce which provide wear protection, high hardness, corrosive resistance, and good adhesion. Recently some works have discussed that multilayer films are possibly better than single layer films used in modern industrial productions due to promising properties. These include metal/metal, metal/ceramic and ceramic/ceramic multilayer systems. Therefore, the multilayer coatings, e.g. TiN/CrN, TiN/ZrN, TiN/NbN, TiN/$Ni_{0.9}Cr_{0.1}$, TaN/NbN, and CrN/NbN have been found to improve mechanical properties, such as wear protection, oxidation and corrosion resistance since the interfaces parallel to the substrate surface acting to deflect cracks or providing barriers to prevent dislocation motion, comparing to single layer coatings. The alternating multilayer design built up the more interfaces which allow cracks to be shifted, thereby dispersing energy and hence improving toughness.

Ananthakumar et al. have shown that a TiN/TiAlN coating have lower friction coefficient and lower wear rate than single layer films. The results of experiments indicates that a TiN/TiAlN multilayer coating have better corrosion resistance in 3.5% NaCl solution. Recent work by Hongx and co-workers has improved the friction and wear properties, and Ti/TiN/DLC (diamond-like carbon) multilayer hard films are fabricated onto bearing steel surface. Result shows that the friction coefficient against steel ball decreases from 0.92 to 0.25, the longest wear life increases nearly by 22 times. Subramanian et al. have shown significant improvement in corrosion resistance in environment which could be achieved by TiN/VN multilayer coatings on steel substrates. The TiN/VN multilayer coated films shows better protective efficiency than the single layer and uncoated ones. Zhao et al. have been found between TiN and (Ti,Al)N layers, at the interface, other layered interfacial place which composes of fine sub-layers by the rotation of the specimen. The hardness values of the multilayers exhibit higher hardness compared with that of monolithic (Ti,Al)N film.

Titanium nitride (TiN) films prepared by PVD processes have been used in engineering applications because of their desirable properties including high hardness, chemical stability, and high toughness. In particular, hard coatings such as TiN have been

applied the protection of tools for forging, machining, and cutting technologies. Niobium nitride (NbN) films can be widely used as numerous applications due to its better wear resistance and high hardness. Though, there are only few information usable on the mechanical properties, most research is focused on superlattice films which are made up of NbN film and other materials together. In the present study, TiN/NbN multilayered thin films are deposited on die steel (SKD11) by D.C. reaction magnetron sputtering. The effects of number of layers on the morphology, microstructure, and mechanical properties of TiN/NbN multilayer films have been investigated by stylus profiler, X-ray diffraction, field-emission scanning electron microscope (FE-SEM), nanoindentation, and pin-on-disk, respectively.

Experimental

1) Coating Deposition Conditions

TiN, NbN single layered coatings and TiN/NbN multilayer films, were deposited on die steel substrate using a reactive D.C. magnetron sputtering. The substrates were then finely polished to 1μm, ultrasonically cleaned in alcohol for 3 min and subsequently blown dry in flowing N_2 gas before deposition. Sputtering targets were pure Ti (99.95%) and Nb (99.95%) which were mounted on the D.C. cathodes durations in high purity Ar (99.999%) and N_2 (99.999%) gas at the ratio of 30/5. The distance between the target and the substrate is approximate 5 cm. Prior to sputtering, a pre-sputtering process was performed for 10 min, to eliminate contamination from the target. The substrate temperature was maintained about 250 ^{o}C, the total pressure was kept at 0.8 Pa, and target power was kept at 200 W. The TiN/NbN multilayer films with thicknesses of about 2 um were prepared. The multilayer films undertook a various layers between 8 and 64.

2) Coating Preparation and Observation Conditions.

The microstructure and composition of TiN/NbN thin films were investigated by X-ray diffraction (XRD). The thickness of all films was carefully measured by stylus profiler (XP-2). The morphology and cross-sectional view of films was observed using field-emission scanning electron microscope (FE-SEM). Nanohardness and Young's modulus of the deposited layers were also examined by means of a nanoindentation technique using nanoindenter (Nano Test) at a load of 5 mN. Hardness analyses also enabled us to determine Young's modulus E for an assumed Poisson's coefficient n. Wear tests were performed on pin-on-disk configuration and unlubricated conditions by using hardened steel ball. The tests times for the slide experiments were 7 min with normal loads of 0.3 kg, respectively.

Results and Discussion

Fig. 1 shows typical XRD pattern of TiN/NbN multilayers deposited at various layers. From the XRD analysis, distinct peaks appear the (111), (200), and (220) crystal orientations of TiN, and the peaks of NbN consistent with (111), (200), (220), and (311) diffractions, respectively. The higher the number of layers leads to increase the crystallization. Besides, TiN shows a (111) preferred growth orientation, and NbN also appears (220) preferential orientation. The phase structure and preferred orientation are similar for the four different layers.

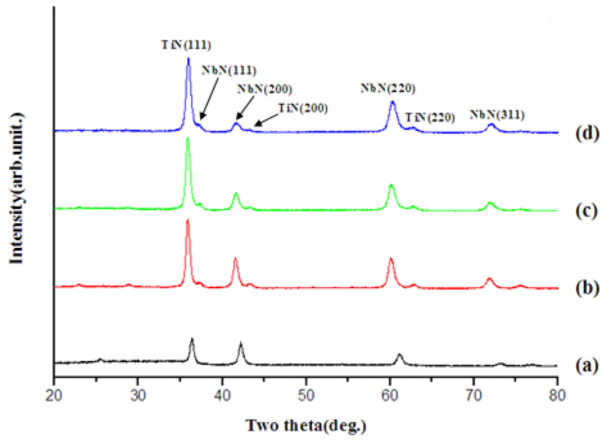


FIG. 1 X-RAY DIFFRACTION PATTERNS FOR THE TIN/NBN FILMS DEPOSITED AT (A) 8 LAYERS (B) 16 LAYERS (C) 32 LAYERS (D) 64 LAYERS

Fig. 2 shows the surface profiler measurements for TiN/NbN multilayer films thickness. The stylus force of 0.05 mg and stylus tip radius of 0.2 μm, are used for the thickness observation. These films deposited on die steel substrate reveal the overall thickness of approximately 2.02 μm and 1.94 μm for different deposition layers. The total thickness of the TiN/NbN multilayer films is approximate 2 μm thick.

The TiN/NbN multilayer films prepared for different total number of layers of 8, 16, 32 and 64 as shown in Fig. 3. SEM images shows lower layers number of TiN/NbN multilayer films has large-grained morphology and loose structure. With increasing layers number, the coating possessed smaller grain structure and the structure became increasingly dense. With the controlling of film layer, the nucleation density of the next material to be deposited increase,

and the number of voids and the void volume fraction at the interfaces decreased. The morphology of grains size has a great effect on mechanical properties. It is almost related to the reduction of grain size, increasing film density, hardness, and elastic recovery.

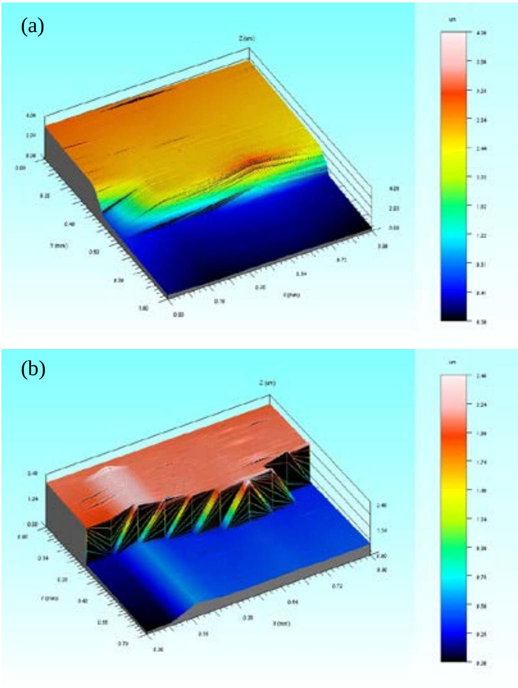


FIG. 2 TYPICAL STYLUS PROFILER IMAGE OF FILMS THICKNESS, USING STYLUS TIP RADIUS =0.2 MM. THE TIN/NBN MULTILAYER FILMS THICKNESS AND LAYERS (A)2.02 MM, 16 LAYERS (B)1.94 MM, 64 LAYERS

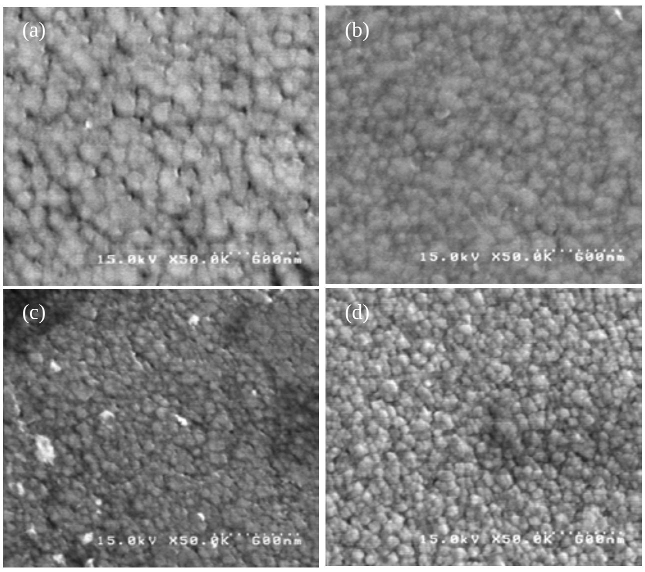


FIG. 3 SEM PHOTOGRAPHS SHOWING THE DEPOSITION FILM SURFACE OF TIN/NBN MULTILAYER FILMS AT (A) 8 LAYERS, (B) 16 LAYERS, (C) 32 LAYERS, AND (D) 64 LAYERS

Switching from the target of titanium and niobium at fixed argon and nitrogen gas flows allow the production of coatings of varying number of titanium and niobium nitride layers, as confirmed by backscattered electron SEM. Fig. 4 and Fig. 5 presents the cross-sectional image of the TiN/NbN multilayer films with different layers. Both 8 and 32 layered TiN/NbN coatings have been taken under investigations. The total thickness of the TiN/NbN multilayer films is near 2 μm. The individual layers (TiN bright, NbN dark) growth shapes and features are visible, and the interface roughness is lowered. TiN/NbN multilayer films are confirmed by using SEM due to the energy of the different electronic emission coefficients for titanium and niobium (atomic number differences).

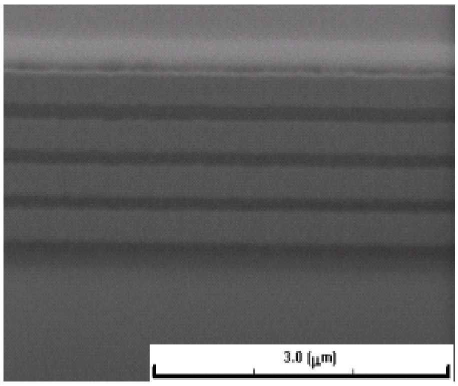


FIG. 4 THE BACKSCATTERED ELECTRON SEM MICROGRAPH ILLUSTRATING THE CROSS- SECTION OF TIN/NBN MULTILAYER FILMS WITH NUMBER OF 8 LAYERS

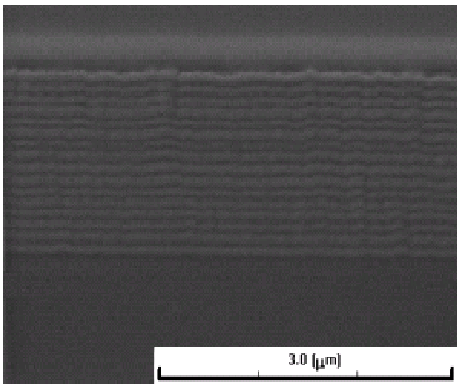


FIG. 5 THE BACKSCATTERED ELECTRON SEM MICROGRAPH ILLUSTRATING THE CROSS- SECTION OF TIN/NBN MULTILAYER FILMS WITH NUMBER OF 32 LAYERS

The nano hardness variation of TiN/NbN multilayers as a function of various layers is shown in Fig. 6. Nano-hardness of the films is measured using a nanoindenter under the applied load of 5 mN. With the increase of the layers, the hardness of TiN/NbN multilayers films is enhanced progressively. The maximum nano-hardness of approximately 23.14 Gpa is observed at the 64 layers. The coherent strain

occurred by lattice mismatch in epitaxial growth can induce changing stress fields which prohibit the generation and motion of dislocations, leading to the strength and hardness increase of the thin films.

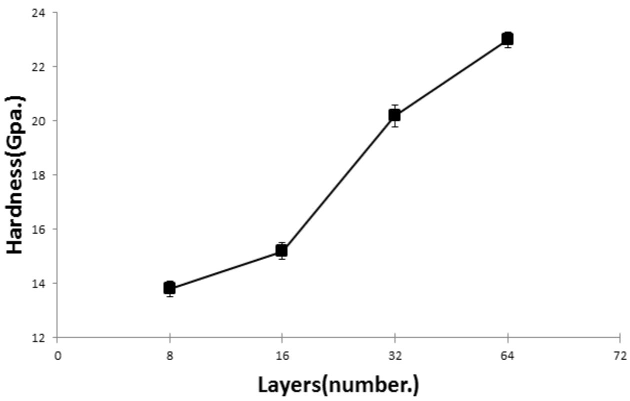


FIG. 6 NANO-HARDNESS VERSUS DIFFERENT LAYERS OF TIN/NBN MULTILAYER FILMS

From the hardness measurements, the Young's modulus E with a various layers is shown in Fig. 7. Since Young's modulus is directly correlated to macroscopic mechanical properties, it can be said that 64 layers appear elastic and harder than those of others. Moreover, the absence of radial cracks on the indentation imprint confirms the plastic character of 64 layers of multilayers. Jensen et al have been found TiN/AlN multilayered structure improves the significance performance like mechanical and tribological properties of single TiAlN. The incorporation of different materials leads to form composite multilayers, which contribute to the higher hardness because of interfacial areas with stress relaxation and lower crack propagation rate.

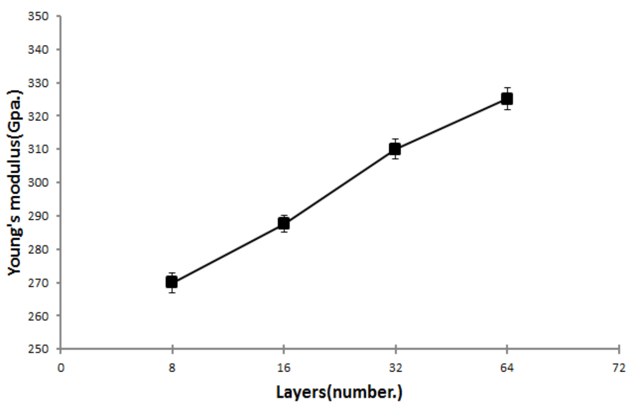


FIG. 7 YOUNG'S MODULUS VERSUS DIFFERENT LAYERS OF TIN/NBN

Typical load-displacement nanoindentation curve of different layers of TiN/NbN multilayered films using the standard indenter is shown in Fig. 8. It can be found that 64 layered TiN/NbN coatings has lower indentation depth in comparison with 8 layers coating. The enhancement in hardness for TiN/NbN multilayer films with layers number increase is attributed to many interfaces that blocked the dislocation movement across interface layer. The dislocation was prevented from gliding across the interfaces and pinning at the interfacial sites.

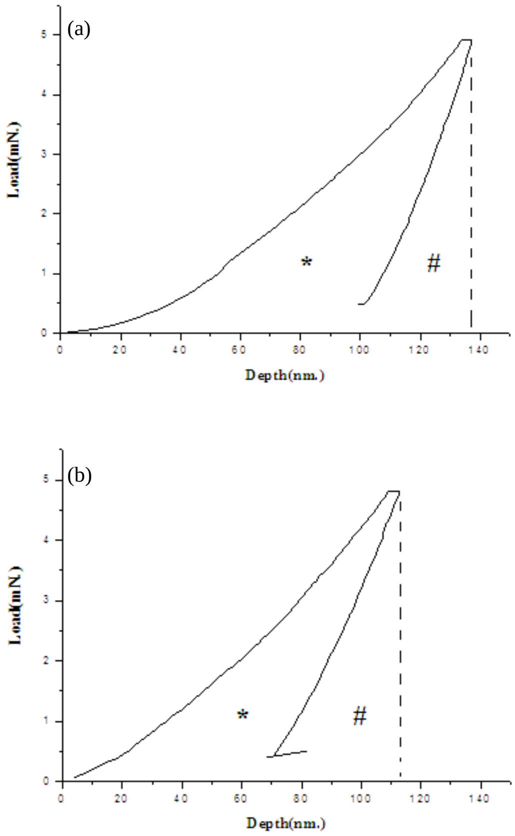


FIG. 8 THE TYPICAL NANOINDENTATION LOAD-DISPLACEMENT CURVES OF TIN/NBN MULTILAYER FILMS WITH OF (A)8 LAYERS AND (B)64 LAYERS

The friction coefficient evolution vs. time for two different layers of TiN/NbN is presented in Fig. 9. In the case of the 8 layered TiN/NbN coatings the friction coefficient in the steady state period presents a mean value of 5.2. However, the 64 layered TiN/NbN coatings show a lower initial friction coefficient about 2.

Fig. 10 shows the average friction coefficient of different samples against steel balls undertaken 75 rpm in circumrotating tribology tests. The number of layers increases resulting in the decrease of the friction coefficient. Moreover, it is interesting to note that the number of 64 layers showed relatively smaller friction coefficients of in comparison with 8 layers coating.

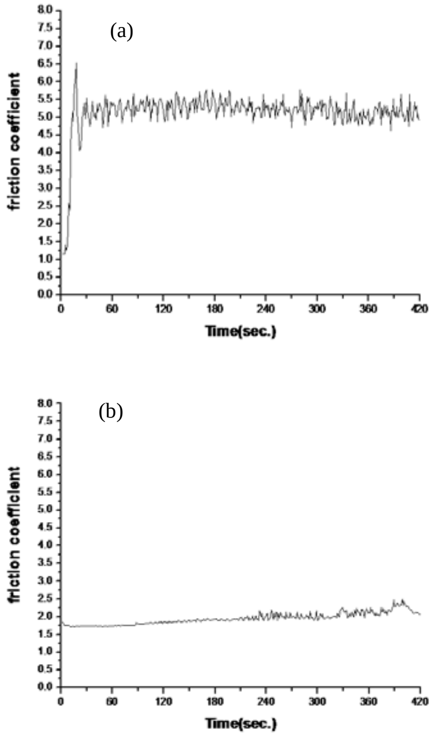


FIG. 9 FRICTION COEFFICIENT VERSUS TIME OF TIN/NBN MULTILAYER FILMS ON BY PIN-ON-DISC (A) 8 LAYERS AND (B) 64 LAYERS

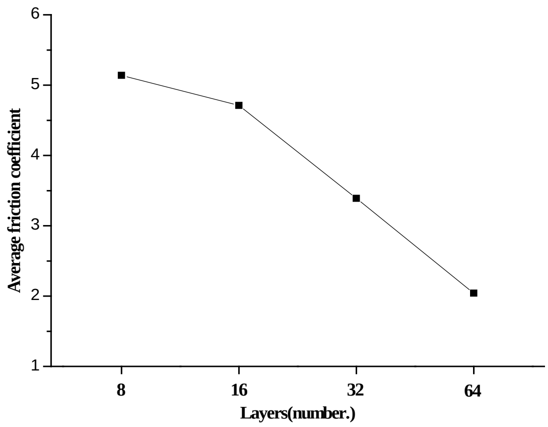


FIG. 10 FRICTION COEFFICIENT VERSUS LAYERS NUMBER OF TIN/NBN MULTILAYER FILMS BY PIN-ON-DISC

Fig. 11 shows the wear depth of TiN/NbN multilayers with different layers number. Pin-on disc/ball-on-disc test is one of the methods used to measure the wear properties of the coatings. Depending on the relative hardness, wear takes place either on the ball or on the coating surface. The coefficient of friction and the wear resistance against corundum body counter are determined as a function of coating composition and strength. The wear depth of coatings decreases with increasing layer number in the coating. The wear of film is the lowest owing to its low coefficient of friction. It could be seen that 64 layers has great wear-resisting. The more is the layer number with a lot of interfaces between layers, which could alter the direction of the initial crack when it permeated deeper into the films. However, interfaces inhibited the dislocations propagation, and the deformation is especially controlled by interfaces boundary moving.

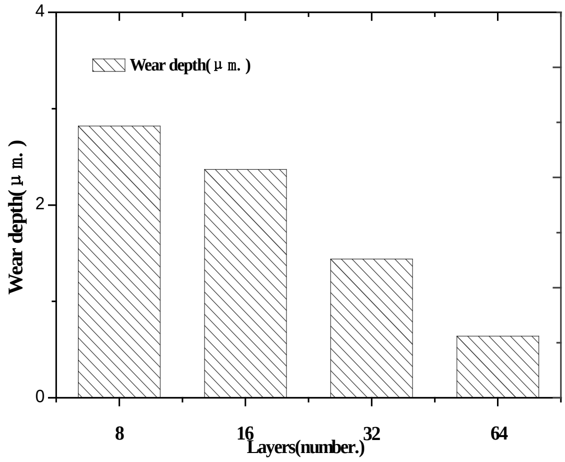
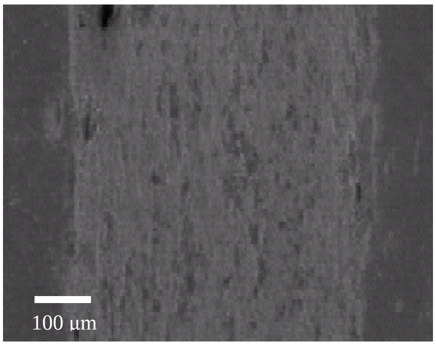


FIG. 11 WEAR DEPTH OF TIN/NBN MULTILAYER FILMS VERSUS DIFFERENT LAYERS

SEM shows 8 layered TiN/NbN coatings of wear tracks on coated disks revealed that clear adhesive wear mechanism was promoted in the contact area during the test (see Fig. 12). SEM and EDS analysis revealed some areas of the worn disc track, where the substrate material was observed and also an adhesive wear mechanism. The EDS analysis performed on the wear track displays the presence a lot of chromium alloy transferred from the ball. In general, wear resistance is proportional to the hardness.

The SEM analysis shows 64 layered TiN/NbN coatings of the worn tracks have been displayed adhesive wear mechanism (see Fig. 13). Furthermore, the EDS carry out on the disc tracks reveal few transfer of material from the ball. Compared to 64 layers, the worn surface of the coating formed at 8 layers shows many micro-cracks perpendicular to the sliding direction. The worn surface explains that the film is brittle and damaging for its wear resistance. The brittleness decreased as the number of layers increased during processing of the coatings. In the case of work materials, such as highly multilayered films which is highly adhesive, providing a lubricative TiN/NbN film on the surface will significantly increase adhesion resistance. Considering the mechanical property, microstructure, and the worn surface characteristics of the coatings, it may be explained the wear behavior of

the coatings. Inspection of the number of 64 layers film shows small wear of the pin and small wear depth of the disk, which shows good mechanical properties.

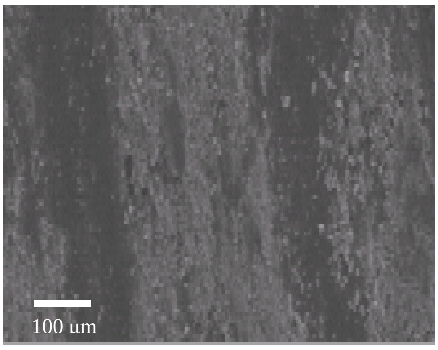


(a)

Element	Wt %	At %
FeK	55.06	63.17
CrK	9.24	11.28
TiK	4.85	6.42
NbL	30.85	19.13
Matrix	Correction	ZAF

(b)

FIG. 12 TYPICAL SEM PHOTOGRAPHS SHOWING THE SCRATCHED CHANNEL OF TIN/NBN 8 MULTILAYER BY PIN-ON-DISK (A) SEM, (B) EDS



(a)

Element	Wt %	At %
FeK	46.66	54.22
CrK	7.82	9.76
TiK	6.43	8.71
NbL	39.09	27.31
Matrix	Correction	ZAF

(b)

FIG. 13 TYPICAL SEM PHOTOGRAPHS SHOWING THE SCRATCHED CHANNEL OF TIN/NBN 64 MULTILAYER BY PIN-ON-DISK (A) SEM, (B) EDS

Conclusions

Using magnetron sputtering method on stainless steel substrates, the TiN/NbN multilayer films with various numbers of layers have been prepared.

X-ray pattern showed that TiN/NbN multilayer films has crystalline phase and preferred orientation.

The number of layers increased resulting in the decrease of grain size to enhance film density and strength.

These multilayer films revealed that the alternating layers amount to 64 had high nano-hardness and good Young's modulus.

The increase of the number of layers improves the abrasive wear behavior of TiN/NbN multilayered films based coatings due to the formation of impeding dislocation motion.

In this work, the friction coefficient decreased substantially with the alternating layers to provide excellent mechanical properties and better performance.

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